First estimation of CH_4 fluxes using the ^{222}Rn Tracer Method over the central Iberian Peninsula

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Abstract

Emissions of CH_4 over the central Iberian Peninsula have been estimated experimentally for the first time using the Radon Tracer Method (RTM), which uses the atmospheric noble radioactive gas ^{222}Rn as an auxiliary tracer. The nocturnal enhancement ratios of atmospheric concentrations of CH_4 and ^{222}Rn, continuously measured at the station of Gredos and Iruelas within the IC3 network since 2012, were used to early estimate the methane emissions in this region by multiplying for a constant radon flux. The possible influence of different methane source areas was observed by footprint analysis of FLEXPART with ECMWF meteorological input at 0.2 degrees horizontal resolution. A linear relationship between atmospheric radon and methane concentrations has been found to occur in 20% of the nocturnal episodes and an average methane emission of 0.12 mg m^{-2} h^{-1} ± 0.03 (1 σ). The data coverage and method is coherent with CH_4 fluxes inferred with the same RTM in Germany, Canada and East Asia and our flux estimates are similar to methane emissions reported by the bottom-up inventory EDGARv4.2 .
Keywords: radon, methane, greenhouse gas, Radon Tracer Method, flux, Flexpart, footprint, inventory.

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1 Introduction

The increase of atmospheric Greenhouse Gases (GHG) is the largest anthropogenic contribution to the additional radiative forcing that mainly drives climate change (IPCC [1]). Their emissions need to be provided separately by each member state under the United Nation Framework Convention on Climate Change. This GHG budgeting is, until now, solely based on bottom-up emission statistics and reports. These estimates are based on the so-called bottom-up approaches, which consist of compiling statistical data on energy use, fuel type and activities and their related emission factors. Nevertheless, these factors for CH_4 emissions and of other non-CO_2 gases are not well known and they have uncertainties of up to 100% (NRC [2]). Established techniques enable of providing independent emission estimates of the fluxes of these gases using available atmospheric observations in order to improve emission inventories (e.g. Vermeulen *et al*. [3]; Jeong *et al*. [4]).

One technique that has been applied and validated for different tracers is the so-called Radon Tracer Method (RTM) (Levin *et al*. [5]), an observation-based method which uses atmospheric measurements of the noble radioactive gas ^{222}Rn and known or assumed values of its flux, in order to retrieve other gases fluxes (e.g. Vogel *et al*. [6]; Wada *et al*. [7]). The natural, radioactive and noble gas ^{222}Rn is nowadays extensively used as tracer for studying a variety of atmospheric processes such as boundary layer characteristics and the exchange of greenhouse gases between the soil surface and the lower troposphere. It is an especially useful tracer because: (i) its only sink in the atmosphere is radioactive decay with a half-time of 3.8 days; (ii) its exhalation over the water is negligible; (iii) its exhalation over the continent can be assumed as constant in a first approximation (Schery and Wasiolek[8]; Zahorowski *et al*. [9]; Szgevary *et al*. [10]; Grossi *et al*. [11, 12]). Since November 2012 measurements of ^{222}Rn concentrations, together with CO_2 and CH_4 concentrations, are performed at Near Real Time at the Gredos and Iruelas station (GIC3) at 20 m agl and at 1440 m asl within the Catalan Institute of Climate Science (IC3), ClimaDat network, which monitors the atmospheric concentrations of greenhouse gases in mountain and coastal sites across Spain (http://climadat.es/). Meteorological parameters, such as ambient air humidity, temperature and wind speed and direction are also measured at GIC3 station.

The present study intends to retrieve a first estimation of methane fluxes in the central Iberian Peninsula using the Radon Tracer Method (e.g. Levin *et al*. [5]) under the specific hypothesis of nocturnal conditions and with a constant radon flux of 100 Bq m^{-2} h^{-1}, as reported for this region in the European radon flux map (Szegvary [10]). Atmospheric concentrations of ^{222}Rn and CH_4 measured at the GIC3 station from during its first 5 months of activity have been used for the RTM analysis. Fluxes of CH_4 obtained by this analysis have been compared with GHGs emission inventories results, such as the EDGAR map (EDGAR [13]) and with results obtained in past studies using the same RTM method. Footprint analysis performed with FLEXPART model v8.2 (Stohl *et al*. [14]; Font *et al*. [15]) at 300m a.g.l. and with ECMWF data were used in order to calculate the catchment areas of methane for episode included in the RTM analysis.

2 Methods: observation and analysis

2.1 Site: Gredos and Iruelas Station (GIC3)

The Gredos and Iruelas station is a mountain site located in the Iberian Peninsula. It is located at 1440 masl and it is part of the IC3 ClimaDat Network, which consists of 8 stations distributed around Spain (www.climadat.es). The GIC3 station is located in the Gredos Natural Park (lat. 40.22º N; long. -5.14º E), in the Spanish central plateau. The Gredos Natural Park is located on a granitic basement which presents high activity levels of ^{228}U and this factor enables large amounts of radon to escape from the deeper soil. The average radon flux within this region is of 90–100 Bq m^{-2} h^{-1} and this values is significantly higher than the average radon flux over Europe, former being around 50 Bq m^{-2} h^{-1} (Szegvary [10]). This region is influenced by strong winds coming from the Atlantic Ocean, characterized by a low radon concentration, and weak wind flows coming from the South of the Peninsula and from its inner regions and which transport radon from remote areas. The nocturnal temperature at this station is low, mainly in the winter season, which leads to a strong atmospheric stability allowing an high nocturnal accumulation of atmospheric gases and therefore high concentrations. In Spain, the main sources of CH_4 are estimated to be due to wetland, enteric fermentation from livestock and solid waste disposal on land (EDGAR [13]). In the Gredos Natural Park, the main natural sources of CH_4 include wetlands and livestock, which are characterized by strong seasonal cycles (Ruiz [16]). Although no big cities are present in the Gredos Natural Park the methane transported under specific meteorological conditions, from landfills located in the cities of Madrid (3.2M population; 605 km^2; 150 km far from GIC3), Valladolid (311K population; 197 km^2; 150 km far from GIC3) and Salamanca (213K population;, 38 km^2; 75 km far from GIC3) may affects the CH_4 signal measured at the GIC3 station.

2.2 Atmospheric observations of CH_4 and ^{222}Rn

Atmospheric CH_4 measurements are performed continuously using a G2301 analyzer (Picarro Inc., USA) at GIC3 since November 2012. This device is based on the cavity ring-down spectroscopy technique (Crosson [17]) and offers simultaneous and precise measurements of CO_2, CH_4 and H_2O. To avoid the negative influence of water on the measurements, the sample air is dried before the analysis through a self-designed system, consisting of a Nafion dryer (model PD-100T-72-MPP; Perma Pure) and a cryotrap. The drying system allows reaching a final water content in the sample lower than 100 ppm. The precision of the Picarro G2301 is calculated by using a target gas which is analyzed for 20 min every day and its average precision being 0.3 ppb for CH_4. The instrument is calibrated every 20 days and its accuracy is below 0.9 ppb for CH_4.

An ARMON radon monitor with a minimum detectable concentration (MDC) of about 150 mBq m^{-3} was installed at GIC3. The monitor is based on ^{218}Po alpha spectrometry, which is collected electrostatically on a passivated implanted detector (Grossi [12]).

2.3 The Radon Tracer Method

In order to indirectly estimate CH_4 fluxes using the observed concentrations of CH_4 and ^{222}Rn at GIC3, we used a box model to describe the atmospheric boundary layer similar to Vogel *et al.* [6]. The main assumption is that the boundary layer is a laterally homogeneous and well mixed box with only a variable vertical height during time, h*(t). This box can mathematically be described by eqn (1), where for any tracer the variation of the concentration during the time $C_i(t)$ is proportional to the flux of the tracer $F_i(t)$ and inversely proportional to the height of the boundary layer $(h^*_i(t))$.

$$\frac{dC_i(t)}{dt} \propto F_i(t) \cdot \frac{1}{h_i^*(t)} \tag{1}$$

This method is applied for data measured under specific conditions of wind when the simple box model can expected to be valid, such as during nocturnal stable episodes with low winds and a linearly correlated atmospheric accumulation of methane and radon concentrations with time. The remaining subset of data is then used to derive CH_4 flux estimates. In this study, 90 nights have been used for the analysis where radon and methane increases show a high linear correlation, with $R^2 > 0.6$. The number of cases is not as high as desired but it is enough for the aim of this study of retrieving a first estimation of the methane emission over this area. The analysis has been applied to the hourly data series of CH_4 and ^{222}Rn.

As a first approximation, the radon flux is assumed constant over the period of analysis and its average value for the Gredos and Iruelas region is taken to be 100 Bq m^{-3} h^{-1}, according to the European radon flux map (Szegvary *et al.* [10]). This is just a simple approximation of the real spatial and temporal variability of the radon flux over regional areas (Grossi *et al.* [11]). However, this variation is not expected to be larger than the standard deviation of the results of the CH_4 fluxes obtained by RTM (Levin *et al.* [5]; Vogel *et al.* [6]; Wada *et al.* [7]) neither larger than uncertainties for regional CH_4 emissions in exiting inventories (NRC [2]; EDGAR [13]) and does not contradict the aim of this study of retrieving a first estimation of the methane flux over the central Iberian Peninsula. Applying eqn (1) for both CH_4 and ^{222}Rn and assuming that they are well mixed in the box boundary layer at any time t, $h^*_{CH4}(t) = h^*_{222Rn}(t)$, as obtained from eqn (2), with a dimensionless conversion factor c derived from the observed slope of the concurrent concentration increase of ^{222}Rn and CH_4.

$$\frac{\frac{dc_{CH_4}(t)}{dt}}{\frac{dC_{222_{Rn}}(t)}{dt}} \cdot F_{222_{Rn}} = c \cdot F_{222_{Rn}} = F_{CH_4} \quad (2)$$

2.4 FLEXPART footprint analysis

The Lagrangian particle dispersion model FLEXPART version 8.2 was used in this study in order to calculate the footprint during the nocturnal episodes selected by the RTM and analyzing the different source contributions. The FLEXPART model has been extensively validated and is nowadays widely used by the scientific community (e.g. Stohl *et al.* [14, 18]; Seibert *et al.* [19]; Arnold *et al.* [20]). The model computes the trajectories of air parcels arriving at the receptor point. These air parcels are represented by 10000 virtual particles which transport and dispersion is modeled using meteorological data by the European Center for Medium-range Weather Forecast (ECMWF). The FLEXPART model has been run for each nocturnal episode, selected for the RTM method at 18h, 21h, 00h, 03h, 06h and 09h UTC in backward mode. Each back-trajectory simulation was run for 4 days with an output for a time-step of 3 hours. The FLEXPART domain was chosen as 0.2 degrees box defined in -40º longitude, 25º latitude for the lowest left corner; 10º lon., 65º lat. for the upper right corner) and a nested domain of 0.05 degrees resolution. The FLEXPART model, furthermore, accounts for the vertical positions of the air parcels and for their residence time. This information allows us to estimate the influence of the local surface fluxes on the observed concentrations when air parcels are closest to the ground. A maximum height of 300 meters has been selected for the footprint analysis following Font et al., 2011. In Figure 1 an example is shown of the main and nested domains used in our FLEXPART runs to calculate the footprint of the GIC3 station.

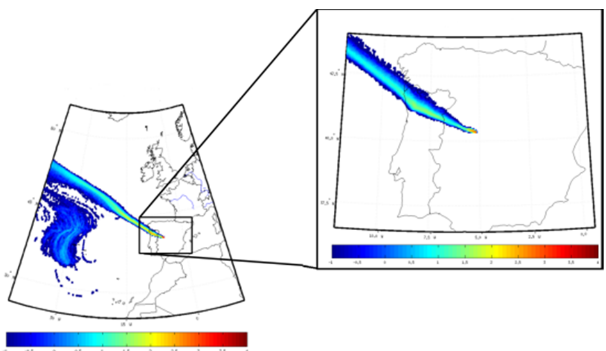

Figure 1: Example of the main and the nest domains used for the footprint analysis of Flexpart 4-d backward simulations up to 300 m height.

3 Results

3.1 Observational data

The atmospheric concentrations of CH_4 and ^{222}Rn measured at the Gredos and Iruelas station from mid-November 2012 to mid-April 2013 were used to apply the RTM method using the radon gas as tracer for a first estimation of the CH_4 fluxes over the central Iberian Peninsula. The data series of atmospheric ^{222}Rn and CH_4 are presented in Figure 2, together with meteorological parameters of humidity, temperature, wind speed and wind direction measured at this station. The GIC3 is a new atmospheric station and only 5 months of data were available for this first analysis. Nevertheless, it allows a first estimation of the CH_4 emission by the RTM. The atmospheric concentrations of the two gases have a coherent behavior both showing a good diurnal-nocturnal variability. An average radon concentration of 5.49 ± 2.25 Bq m^{-3} was measured during this period. The lowest concentration (of about 0.5 Bq m^{-3}) was observed with the air flow coming from 300º, in corresponding to an Atlantic Ocean origin and with high wind velocity (around 7 m s^{-1}). The air masses coming from the ocean are poor in radon and a strong atmospheric mixing further dilutes its atmospheric concentration. The highest concentrations of radon (of about 30 Bq m^{-3}) were observed during accumulation episodes with weak local winds, which lead to the increase of ^{222}Rn concentration in the lower layer of the atmosphere due to its exhalation from local areas. Average concentrations of CH_4 of 1.897 ppm have been measured at the GIC3 with minimum values of 1.836 ppm and a maximum value of 2.152 ppm. During the first week of December 2012 both ^{222}Rn and CH_4 showed high atmospheric concentrations apparently related to local stable conditions which favor their accumulation in the lower boundary layer (Figure 2). At the end of February 2013 there is a departure between the concentration time-series of the two gases; the atmospheric concentrations of radon decreasing due to the strong wind arriving at the GIC3 while the concentration of CH_4 increasing. This fact could be due to distant emissions of methane which are transported to the GIC3 station by strong advective winds (Figure 2).

3.2 RTM-based CH_4 fluxes

The application of the RTM for an early observation-based estimation of the methane emission over the central Iberian Peninsula was carried out assuming a constant radon flux over this region of 100 Bq m^{-2} h^{-1}, such as reported in the European radon flux inventory by Szegvary *et al.* [10]. Using the weekly flux map of Szegvary *et al.* [10] and our FLEXPART modelling results, we found an average (continental) radon flux in the footprint of the Gredos site of 97 Bq m^{-2} h^{-1} with a standard deviation of 13 Bq m^{-2} h^{-1}.

The method selects the nights where the gases showing a high linear correlation ($R^2 > 0.6$, $p < 0.05$). In each one of these episodes, the variation of the atmospheric concentrations of both gases between 18h and 06h were used

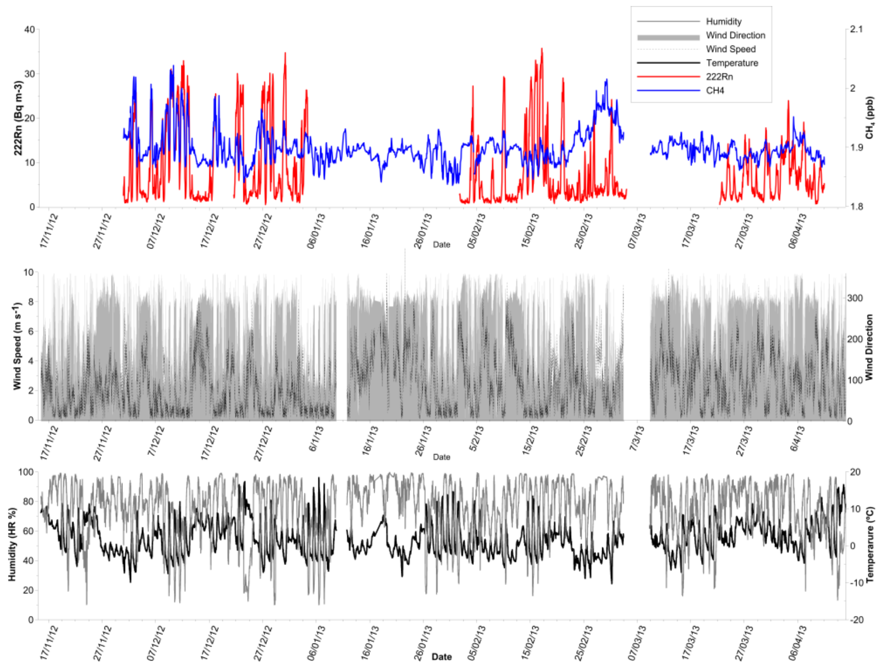

Figure 2: Time series of atmospheric concentrations of CH_4 (blue line in the upper panel) and ^{222}Rn (red line in the upper panel) measured at GIC3 station between mid-November 2012 and mid-April 2013 together with other meteorological parameters (temperature, black line in the bottom panel; relative humidity, grey line in the bottom panel; wind speed, black line in the central panel; wind direction, grey filling in the central panel).

(c.f. eqn. (2)) in order to calculate the night-time methane flux. Results of CH_4 fluxes obtained by RTM analysis in GIC3 are presented in Figure 3. The results show an inter-quartiles (IQR) range of 0.09-0.24 mg m^{-2} h^{-1} and a mean value of 0.12 ± 0.03 (1σ) mg m^{-2} h^{-1}. Although the flux density depends on the catchment area and cannot be directly compared for different sites, the results of this study are similar in magnitude to the results obtained by other researchers using the RTM methods: (i) for Germany, where mean values of 0.86 ± 0.24 mg m^{-2} h^{-1} were derive from observation time series between 1995-1997 and of 0.72 ± 0.43 mg m^{-2} h^{-1} using atmospheric gases concentrations from 1996 and 2008 (Levin *et al*. [5, 21]); (ii) for Canada, where Vogel [6] found an inter-quartiles range in the South of Ontario of 0.19-0.49 mg m^{-2} h^{-1} with time series data from 2006-2009; (iii) for the East of Asia, where Wada *et al.* [7] have estimated RTM-based fluxes of CH_4 of 0.53 ± 0.13 mg m^{-2} h^{-1} and 0.87 ± 0.13 mg m^{-2} h^{-1} respectively in the islands of Minamitorishima and of Yonagunijima in Japan and using observation data from 2007–2011. However, the mean value of CH_4 flux RTM-based calculated in this study is lower than the ones retrieved in the other previous studies in agreement with the difference observed in the methane emission estimated for each country in the EDGAR inventory. Results obtained in this study have been compared with bottom-up statistics from EDGAR. The total CH_4 emissions for each year, for each sector and for each country are available in the EDGAR inventory with a grid resolution of 0.1 degree (EDGAR [13]). The reported flux density in the EDGAR inventory over the region of the GIC3 station for 2008 show an average value of 0.06 mg m^{-2} h^{-1} and an increase over the time of only 1% per year for Spain. This value is lower than the mean flux estimated for our data set 2012–2013 in GIC3, however, similar to the CH_4 emissions RTM-based values we obtained during February 2013 as seen in Figure 3. Indeed, the results in Figure 3 show three main CH_4 fluxes groups which have been observed and that are linked to the variation of the catchment area of methane arriving at GIC3 station.

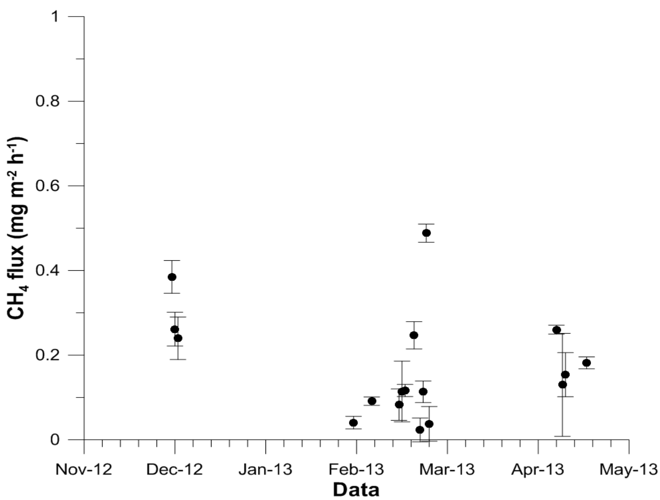

Figure 3: Results of RTM-based CH_4 fluxes (mg m^{-2} h^{-1}) obtained at Gredos and Iruelas station from December 2012 to April 2013.

In December 2012 the average CH_4 flux obtained by RTM analysis is 0.26 ± 0.04 mg m^{-2} h^{-1}. This value is significantly higher than the one obtained by the EDGAR inventory map. Footprint analysis of air masses arriving at GIC3 during these episodes and in contact with the soil, performed by FLEXPART 4-days backward simulations, show a catchment area including the north of Portugal and north-west of Spain for these episodes (Figure 4a)). The EDGAR map for this area for 2008 shows values of CH_4 fluxes between 0.82 and 1.04 mg m^{-2} h^{-1}. In the end of February 2013 most of the selected night events give low CH_4 flux with a mean of 0.09 ± 0.04 mg m^{-2} h^{-1}. The footprint analysis for these episodes show air masses coming from the south of the Iberian Peninsula as reported in the example in Figure 4b). The EDGAR emission map for this area shows lower values than in the north-west of the Peninsula and that range between 0.08–0.42 mg m^{-2} h^{-1}. Finally, in April 2013 the average CH_4 emissions estimated by RTM in GIC3 have a mean value of 0.17 ± 0.03 mg m^{-2} h^{-1}. A typical example of footprint analysis of air masses arriving at GIC3 station during these nights is shown in Figure 4c). Air masses in contact with the soil are arriving from the north of the Iberian Peninsula where the EDGAR emissions map shows values of CH_4 flux ranging between 0.08–0.4 mg m^{-2} h^{-1}.

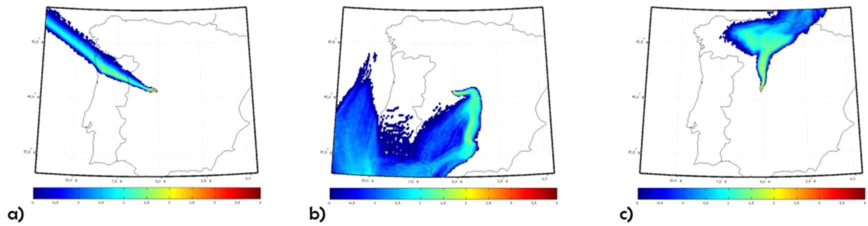

Figure 4: Example of the main residence time of atmospheric simulated particles arriving at GIC3 at 00 UTC on 5 December 2012 (a); 12 February 2013 (b); 14 April 2013 (c). Footprints analysis done with Flexpart 4-d backward simulations until a height of 300m.

4 Conclusion

The atmospheric concentrations of CH_4 and ^{222}Rn measured continuously at the Gredos and Iruelas station, included in the IC3 Network and located in the central Spanish plateau, have been used to test the utility of the observation-based Radon Tracer Method and retrieve an early estimation of the CH_4 flux in the Central Iberian Peninsula. In agreement with past studies the RTM has been applied using a constant radon flux over the region of interest of 100 Bq m^{-2} h^{-1}. The 20% of the total available data were used in this analysis because the threshold for the linear correlation between atmospheric concentration of CH_4 and ^{222}Rn was set high (i.e. $R^2>0.6$) to ensure more reliable results. The flux estimates have an inter-quartile range of 0.09-0.24 mg m^{-2} h^{-1} and a mean value of 0.12 ± 0.03 (1σ) mg m^{-2} h^{-1}. This value is higher than the emissions reported in this area in the EDGAR inventory map that reports an average flux density of 0.06 mg m^{-2} h^{-1} for 2008 and an increase over time of 1% per year for Spain. Nevertheless, the RTM-based emissions obtained in this study are similar in magnitude to the CH_4 fluxes obtained by other studies over the world, by means of the same radon tracer method. Its mean value is lower than the ones obtained in the other studies these values are in agreement with the total emissions estimated for each country in the EDGAR inventory. In addition, FLEXPART footprint analysis carried out for the nights included in the RTM analysis show different possible catchment areas in the north-west, the south and the north of the Iberian Peninsula, a fact that justifies the variation observed in the RTM-based CH_4 flux in the GIC3 region. The estimated CH_4 flux increases when the catchment area includes the north of Portugal and Galicia region with a mean value of 0.26 ± 0.04 mg m^{-2} h^{-1}. A mean CH_4 flux of 0.09 ± 0.04 mg m^{-2} h^{-1} is found when the catchment area is centered over the south of the Iberian Peninsula and average CH_4 emission estimates by RTM at GIC3 yield a mean value of 0.17 ± 0.03 mg m^{-2} h^{-1} when the air masses coming from the north of the country are influencing the measurements at GIC3. These variations are in agreement with the magnitude and general spatial distribution of CH_4 emissions in the bottom-up dataset (EDGAR V4.2) for those three areas. This first study was applied for only 90 nights and only the 20% of them fulfilled the RTM requirements. Furthermore, an assumption of constant radon fluxes was applied in the analysis although variations of the radon flux on both temporal and spatial scale are nowadays accepted. The RTM method is going to be applied to the GIC3 region using large datasets and including the radon flux variability over this area in order to improve the statistical analysis and to retrieve seasonal variability estimates of the methane fluxes. Nevertheless the present results of the CH_4 fluxes offers for the first time experimental of CH_4 fluxes over the Iberian Peninsula, that are coherent with past results from literature. The difference observed in the CH_4 flux together with information coming from the footprint analysis and the EDGAR inventory allow understanding the influence of the catchment areas on the gases concentrations observed at GIC3 and highlight the importance of better characterizing these possible sources. The availability of good atmospheric data and the RTM analysis represent a fast and reliable estimation of greenhouse gases.

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